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Time-dependent current-density-functional theory for metals

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Chapter 4

Relativistic DFT

Systems of heavy atoms are not correctly described within a nonrelativistic quantum-mechanical model. In this case one has to consider the Dirac equation, which satisfies both the postulates of special relativity and those of quantum mechanics. In this chapter we give the main concepts of a relativistic density functional formulation and how to reduce the four-component Dirac-Kohn-Sham equations to two-component pseudorelativistic equations. We discuss in particular the two-component equations within the zeroth-order regular approximation, we extend this formulation to the time-domain, and we combine it with our formulation of linear response.

4.1 RDFT from quantum electrodynamics

The appropriate starting point for a fully relativistic description of the electronic structure of atoms, molecules, clusters, and solids is Quantum Electrodynamics (QED). However, in general, the QED equations represent a quite complex computational problem, thus approximations are unavoidable. An approximation is the Dirac equation. The quantum-mechanical evolution of a system of N interacting electrons in the presence of time-dependent scalar and vector potentials $v(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$, respectively, is described by the following Hamiltonian,

$$\sum_i^N (c\boldsymbol{\alpha} \cdot \boldsymbol{\pi}_i + \beta c^2 + v(\mathbf{r}_i, t)) + \sum_{i < j} U(\mathbf{r}_i - \mathbf{r}_j), \quad (4.1)$$

with $U(\mathbf{r}_i - \mathbf{r}_j)$ the electron-electron interaction and βc^2 the rest mass of the electron. Here $\boldsymbol{\pi}_i = \mathbf{p}_i + \mathbf{A}(\mathbf{r}_i, t)/c$, $\boldsymbol{\alpha}$ is the velocity operator,

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad (4.2)$$

with $\boldsymbol{\sigma}$ the vector of two-by-two Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (4.3)$$

and β is the four-by-four matrix

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad (4.4)$$

with I the two-by-two identity matrix. The Dirac Hamiltonian can, thus, be expressed as a four-by-four matrix which operates on the wavefunction Ψ . This means that solution of Eq. (4.1) leads to four-component wavefunctions or spinors. The Dirac equation admits both positive energy solutions, associated with electrons, and negative energy solutions, associated with positrons, i.e. particles with the same mass as the electrons, but opposite charge. Normally one is interested in the electronic states. If the rest mass energy for positive energy states is subtracted from the Dirac equation (change of gauge), the solutions of interest are those in which the upper two-component spinor of the wavefunction is predominant. This component is called large component, while the lower two-component spinor is called small component. The electron and positron states can be completely decoupled by means of unitary transformations, as, for example, the Fouldy-Wouthuysen transformation. The electronic states are then described by a two-component Hamiltonian.

4.1.1 The stationary and time-dependent Dirac-Kohn-Sham equations

Relativistic density functional theory (RDFT) has been formulated within the framework of quantum electrodynamics, where the renormalization procedure provides a minimum principle which makes possible the relativistic extension of the Hohenberg-Kohn theorem [73]. Recent reviews of the quantum electrodynamical basis of RDFT have been given by Engel *et al.* in Refs [74, 75]. Using the renormalized ground-state energy E_{0R} and the ground-state four-current $j_R^\mu(\mathbf{r})$, one can then prove that there exists a one-to-one correspondence between the class of external potentials just

differing by gauge transformations, $V_{ext}^\mu(\mathbf{r}) = (v_{ext}(\mathbf{r}), \mathbf{A}_{ext}(\mathbf{r}))$, ($\mu = 0, 1, 2, 3$), the associated class of (nondegenerate) ground-state wavefunctions $|\Phi_0\rangle$, and ground-state four-current $j_R^\mu(\mathbf{r})$. This means that the ground-state wavefunction is a unique (and universal) functional of the ground-state four-current. As consequence, also the ground-state energy of the system is a functional of the ground-state current, $E_{0R}[j_R]$. The exact $j_R^\mu(\mathbf{r})$ minimizes $E_{0R}[j_R]$ under the condition of current conservation, and thus conservation of the total charge Q ,

$$\sum_{\mu} \partial_{\mu} j_R^{\mu}(\mathbf{r}) = 0, \quad (4.5)$$

$$\frac{1}{c} \int j_R^0(\mathbf{r}) d\mathbf{r} = Q, \quad (4.6)$$

where we use the notation $\partial_{\mu} = (\partial_t/c, \nabla)$. In order to derive the relativistic Kohn-Sham equations [76, 77] one has to assume the existence of an auxiliary system of noninteracting particles in effective potentials $V_s^\mu(\mathbf{r})$ with exactly the same ground-state four-current as the interacting system. This assumption has not been examined in the relativistic case, but one expects analogous statements as in the nonrelativistic case. Within the relativistic Kohn-Sham scheme the ground-state four-current and energy can be represented in terms of auxiliary single-particle four-spinors ψ_i . This representation in general also includes vacuum polarization contributions. However, for most RDFT applications these electrodynamical effects are irrelevant, thus we will neglect them in the following for simplicity (no-pair approximation) [74, 75]. The four-current can then be expressed as

$$j^\mu(\mathbf{r}) = c \sum_{-mc^2 < \epsilon_i \leq \epsilon_F} \psi_i^\dagger(\mathbf{r}) \alpha^\mu \psi_i(\mathbf{r}), \quad (4.7)$$

where ϵ_F is the Fermi level of the auxiliary system and the summation is over the electronic states. In (4.7) the symbol “ \dagger ” indicates the Hermitian adjoint, and $\alpha^\mu = (\alpha^0, \boldsymbol{\alpha})$ is a four-vector of four-by-four matrices, with $\alpha^0 = I$ the identity matrix and $\boldsymbol{\alpha}$ given in (4.2). Within the Kohn-Sham scheme the total ground-state energy functional $E_0[j^\mu]$ can be decomposed in terms of the kinetic energy of the auxiliary system, $T_s[j^\mu]$, the external potential energy, $E_{ext}[j^\mu]$, the Hartree energy, $E_H[j^\mu]$, and the exchange-correlation functional, $E_{xc}[j^\mu]$,

$$E_0[j^\mu] = T_s[j^\mu] + E_{ext}[j^\mu] + E_H[j^\mu] + E_{xc}[j^\mu]. \quad (4.8)$$

The minimization of the total ground-state energy $E_0[j^\mu]$ with respect to the single-particle four-spinors ψ_k leads to the Dirac-like relativistic KS-equations [74, 75],

$$\{c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \beta c^2 + v_s(\mathbf{r})\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (4.9)$$

where $\boldsymbol{\pi} = \mathbf{p} + \mathbf{A}_s(\mathbf{r})/c$. The Kohn-Sham four-potential $V_s^\mu(\mathbf{r}) = (v_s(\mathbf{r}), \mathbf{A}_s(\mathbf{r}))$ consists of the external, the Hartree, and the exchange-correlation four-potentials, respectively,

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}), \quad (4.10)$$

$$\mathbf{A}_s(\mathbf{r}) = \mathbf{A}_{ext}(\mathbf{r}) + \frac{1}{c} \int d\mathbf{r}' \frac{\mathbf{j}_T(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mathbf{A}_{xc}(\mathbf{r}), \quad (4.11)$$

where $\mathbf{j}_T(\mathbf{r}')$ is the transverse current-density (see chapter 2). Here the exchange-correlation four-potential $V_{xc}^\mu(\mathbf{r}) = (v_{xc}(\mathbf{r}), \mathbf{A}_{xc}(\mathbf{r}))$ is defined by the relation

$$\lim_{\lambda \rightarrow 0} \frac{E_{xc}[j^\mu + \lambda \delta j^\mu] - E_{xc}[j^\mu]}{\lambda} = \int V_{xc}^\mu(\mathbf{r}) \delta j^\mu(\mathbf{r}) d\mathbf{r}, \quad (4.12)$$

where $V_{xc}^\mu(\mathbf{r})$ is determined up to a gauge transformation $V_{xc}^{\mu'}(\mathbf{r}) \rightarrow V_{xc}^\mu(\mathbf{r}) + \delta_\mu \Lambda_{xc}(\mathbf{r})$ as

$$\begin{aligned} \int V_{xc}^{\mu'}(\mathbf{r}) \delta j^\mu(\mathbf{r}) d\mathbf{r} &= \int V_{xc}^\mu(\mathbf{r}) \delta j^\mu(\mathbf{r}) d\mathbf{r} - \int \Lambda_{xc}(\mathbf{r}) (\delta_\mu \delta j^\mu(\mathbf{r})) d\mathbf{r} \\ &= \int V_{xc}^\mu(\mathbf{r}) \delta j^\mu(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (4.13)$$

Here we have used the condition of current conservation given in (4.5). The set of Eqs (4.7), (4.9)-(4.11) has to be solved self-consistently in order to obtain the exact four-current $j^\mu(\mathbf{r})$ of the interacting system. One can extend Eq. (4.9) to the time-domain [78],

$$\{c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \beta c^2 + v_s(\mathbf{r}, t)\} \psi_i(\mathbf{r}, t) = i \frac{\partial}{\partial t} \psi_i(\mathbf{r}, t), \quad (4.14)$$

where $\boldsymbol{\pi} = \mathbf{p} + \mathbf{A}_s(\mathbf{r}, t)/c$. The four-component current $j^\mu(\mathbf{r}, t)$ is now time-dependent and it is given by

$$j^\mu(\mathbf{r}, t) = c \sum_i \psi_i^\dagger(\mathbf{r}, t) \boldsymbol{\alpha}^\mu \psi_i(\mathbf{r}, t), \quad (4.15)$$

where the summation is over states which represent the evolution of the initial occupied electronic states with energies $-mc^2 < \epsilon_i \leq \epsilon_F$. The scalar component of the four-current is the density,

$$\rho(\mathbf{r}, t) = j^0(\mathbf{r}, t)/c = \sum_i \psi_i^\dagger(\mathbf{r}, t) \psi_i(\mathbf{r}, t), \quad (4.16)$$

whereas the vector component is

$$\mathbf{j}(\mathbf{r}, t) = c \sum_i \psi_i^\dagger(\mathbf{r}, t) \boldsymbol{\alpha} \psi_i(\mathbf{r}, t), \quad (4.17)$$

where we have used the notation $j^\mu = (c\rho, \mathbf{j})$.

4.1.2 Gordon decomposition of the four-current

To keep contact with the nonrelativistic density functional approaches, we can make more explicit the content of the vector current by using the Gordon decomposition. We rewrite the expression of the vector current as

$$\mathbf{j}(\mathbf{r}, t) = c \sum_i \left(\frac{1}{2} \psi_i^\dagger(\mathbf{r}, t) \boldsymbol{\alpha} \psi_i(\mathbf{r}, t) + \frac{1}{2} \psi_i^\dagger(\mathbf{r}, t) \boldsymbol{\alpha} \psi_i(\mathbf{r}, t) \right), \quad (4.18)$$

and the time-dependent DKS equation (4.14) as

$$\psi_i(\mathbf{r}, t) = -\frac{1}{c} \beta \boldsymbol{\alpha} \cdot \boldsymbol{\pi} \psi_i(\mathbf{r}, t) + \frac{i\partial/\partial t - v_s(\mathbf{r}, t)}{c^2} \beta \psi_i(\mathbf{r}, t). \quad (4.19)$$

We can then substitute Eq. (4.19) into the first term on the right-hand side of Eq. (4.18), and its Hermitian adjoint into the second term. After some elementary rearrangements exploiting the properties of the matrices $\boldsymbol{\alpha}$ and β , we arrive at

$$\mathbf{j}(\mathbf{r}, t) = \mathbf{j}_p(\mathbf{r}, t) + \mathbf{j}_d(\mathbf{r}, t) + \nabla \times \mathbf{s}(\mathbf{r}, t) + \frac{\partial \mathbf{g}(\mathbf{r}, t)}{\partial t}, \quad (4.20)$$

with

$$\mathbf{j}_p(\mathbf{r}, t) = -\frac{i}{2} \sum_i (\psi_i^\dagger(\mathbf{r}, t) \cdot \beta \nabla \psi_i(\mathbf{r}, t) - \nabla \psi_i^\dagger(\mathbf{r}, t) \cdot \beta \psi_i(\mathbf{r}, t)), \quad (4.21)$$

$$\mathbf{j}_d(\mathbf{r}, t) = \frac{1}{c} \mathbf{A}_s(\mathbf{r}, t) \sum_i \psi_i^\dagger(\mathbf{r}, t) \beta \psi_i(\mathbf{r}, t), \quad (4.22)$$

$$\mathbf{s}(\mathbf{r}, t) = \frac{1}{2} \sum_i \psi_i^\dagger(\mathbf{r}, t) \cdot \beta \boldsymbol{\Sigma} \psi_i(\mathbf{r}, t), \quad (4.23)$$

$$\mathbf{g}(\mathbf{r}, t) = -\frac{i}{2c} \sum_i \psi_i^\dagger(\mathbf{r}, t) \cdot \beta \boldsymbol{\alpha} \psi_i(\mathbf{r}, t). \quad (4.24)$$

The four-by-four matrix $\boldsymbol{\Sigma}$ in (4.23) is defined as

$$\boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}. \quad (4.25)$$

We can conclude that the vector current can be split into the paramagnetic and diamagnetic components $\mathbf{j}_p(\mathbf{r}, t)$ and $\mathbf{j}_d(\mathbf{r}, t)$, a spin contribution expressed as curl of the spin density $\mathbf{s}(\mathbf{r}, t)$, and a term which couples large and small components of the DKS wavefunction. Two important considerations on Eq. (4.20) need to be mentioned. First, the contribution to the current due to the term $\partial \mathbf{g}(\mathbf{r}, t)/\partial t$ is of the order of c^{-1} , unlike the other contributions which are of the order of 1, and it even

vanishes for stationary systems. The other important point, more subtle, is that only the Dirac-Kohn-Sham total current is the same as in the real system, while the various Dirac-Kohn-Sham terms in which the current can be decomposed do not necessarily have any physical meaning.

4.2 The ZORA equations

Fully relativistic calculations based on a four-component Hamiltonian are time-consuming. Several two-component formalisms have been developed and one of the most simple and elegant approaches is the zeroth-order regular approximation (ZORA) [79, 80].

4.2.1 Time-independent case

After the gauge transformation $v_s \rightarrow v_s - c^2$, the one-electron Dirac-Kohn-Sham equation for the large and small components of the four-component wavefunction can be written as follows,

$$\begin{pmatrix} v_s & c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \\ c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} & v_s - 2c^2 \end{pmatrix} \cdot \begin{pmatrix} \phi \\ \chi \end{pmatrix} = \epsilon \begin{pmatrix} \phi \\ \chi \end{pmatrix}. \quad (4.26)$$

A two-component Hamiltonian for electronic states can be generated by finding a unitary transformation U ,

$$U = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}} X^\dagger \\ -\frac{1}{\sqrt{1+X X^\dagger}} X & \frac{1}{\sqrt{1+X X^\dagger}} \end{pmatrix}, \quad (4.27)$$

with $U^{-1} = U^\dagger$, that reduces the Dirac Hamiltonian to a block diagonal form. Foldy and Wouthuysen introduced a systematic method for progressively decoupling large and small components [81]. The transformed Hamiltonian $U \hat{H}^D U^{-1}$ is block-diagonal if we choose \hat{X} to satisfy

$$-\hat{X} v_s - \hat{X} c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} + c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} + (v_s - 2c^2) \hat{X} = 0. \quad (4.28)$$

The upper-left block is the Foldy-Wouthuysen Hamiltonian \hat{H}^{FW} ,

$$\begin{aligned} \hat{H}^{FW} &= \frac{1}{\sqrt{1+\hat{X}^\dagger \hat{X}}} \times (c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} + \hat{X}^\dagger c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} - 2c^2 \hat{X}^\dagger \hat{X} + v_s + \hat{X}^\dagger v_s \hat{X}) \times \\ &\quad \frac{1}{\sqrt{1+\hat{X}^\dagger \hat{X}}}. \end{aligned} \quad (4.29)$$

The Foldy-Wouthuysen equation,

$$H^{FW}\Phi^{FW} = \epsilon\Phi^{FW}, \quad (4.30)$$

has the same one-electron energies ϵ as the Dirac equation, but generates only the positive energy spectrum. The wavefunction Φ^{FW} is a two-component wavefunction that can be related to the large and small components using

$$\begin{pmatrix} \Phi^{FW} \\ 0 \end{pmatrix} = U \begin{pmatrix} \phi \\ \chi \end{pmatrix}, \quad (4.31)$$

so that,

$$\Phi^{FW} = \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}} \phi + \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}} \hat{X}^\dagger \chi, \quad (4.32)$$

$$0 = -\frac{1}{\sqrt{1 + \hat{X} \hat{X}^\dagger}} \hat{X} \phi + \frac{1}{\sqrt{1 + \hat{X} \hat{X}^\dagger}} \chi. \quad (4.33)$$

The last equation is an identity if the operator \hat{X} satisfies $\chi = \hat{X}\phi$. One can then obtain an expression for this operator from the Dirac equation for the small component in (4.26),

$$\chi = \frac{1}{2c^2 + \epsilon - v_s} c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \phi = \hat{X}\phi, \quad (4.34)$$

where \hat{X} automatically satisfies the condition (4.28). If we considered $1/\sqrt{1 + \hat{X}^\dagger \hat{X}} = \sum_{n=0}^{\infty} a_n (\hat{X}^\dagger \hat{X})^n$, and we approximate \hat{X} by expanding the energy-dependent expression $(2c^2 + \epsilon - v_s)^{-1} c\boldsymbol{\sigma} \cdot \boldsymbol{\pi}$ in $\epsilon/(2c^2 - v_s)$, then the Foldy-Wouthuysen Hamiltonian will give at zeroth order the ZORA (zeroth-order regular approximation) Hamiltonian H^{ZORA} ,

$$\hat{H}^{ZORA} = \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \frac{c^2}{2c^2 - v_s} \boldsymbol{\sigma} \cdot \boldsymbol{\pi} + v_s. \quad (4.35)$$

Note that the $\epsilon/(2c^2 - v_s)$ expansion is valid for Coulomb-like potentials everywhere, provided that the energy of the particle is not too large, $\epsilon < (2c^2 - v_s)$, as it is always the case for chemical applications. Another important observation is that by making the zeroth-order regular approximation for the operator \hat{X} , the unitary transformation U is correct only to order $\epsilon/(2c^2 - v_s)$. Thus the transformed Hamiltonian is not exactly block-diagonal, but there is a residual coupling that we neglect. The small component are not completely annihilated as we have assumed in Eq. (4.31). The

ZORA kinetic operator $T^{ZORA} = \boldsymbol{\sigma} \cdot \boldsymbol{\pi} c^2 / (2c^2 - v_s) \boldsymbol{\sigma} \cdot \boldsymbol{\pi}$ can be split into a scalar and a two-component part, so that the one-electron ZORA equation can be written as,

$$\left\{ \boldsymbol{\pi} \cdot \frac{K(\mathbf{r})}{2} \boldsymbol{\pi} + \frac{K^2(\mathbf{r})}{4c^2} \boldsymbol{\sigma} \cdot [\nabla v_s \times \boldsymbol{\pi}] - \frac{1}{c} \frac{K(\mathbf{r})}{2} \boldsymbol{\sigma} \cdot \mathbf{B}_s + v_s \right\} \Phi^{ZORA} = \epsilon \Phi^{ZORA}, \quad (4.36)$$

where $K(\mathbf{r}) = (1 - v_s(\mathbf{r})/2c^2)^{-1}$ and $\mathbf{B}_s = \nabla \times \mathbf{A}_s$. The ZORA one-particle wavefunctions Φ^{ZORA} are two-component spinors and represent the electron-like solutions of the Dirac four-component wavefunctions. The last two terms in the equation represent the spin-orbit coupling and the coupling between the spin and the magnetic field, respectively.

4.2.2 Time-dependent case

If we want to derive the ZORA equation for time-dependent problems, we have to start from the time-dependent Dirac equation,

$$\hat{H}^D \psi(\mathbf{r}, t) = i \partial_t \psi(\mathbf{r}, t), \quad (4.37)$$

where we use the notation $\partial_t = \partial/\partial t$. The equations for the large and small components are as follows,

$$v_s \phi + c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \chi = i \partial_t \phi, \quad (4.38)$$

$$c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \phi + (v_s - 2c^2) \chi = i \partial_t \chi. \quad (4.39)$$

If we express the small component in term of the large component as $\chi = \hat{X} \phi$, Eqs (4.38)-(4.39) become

$$(v_s + c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X}) \phi = i \partial_t \phi, \quad (4.40)$$

$$\begin{aligned} (c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} + (v_s - 2c^2) \hat{X}) \phi &= i \partial_t (\hat{X} \phi) \\ &= [i \partial_t, \hat{X}] \phi + i \hat{X} \partial_t \phi. \end{aligned} \quad (4.41)$$

By substituting Eq. (4.40) in Eq. (4.41) we arrive at the following equation of motion,

$$c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} + [v_s - i \partial_t, \hat{X}] - 2c^2 \hat{X} - \hat{X} c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} = 0. \quad (4.42)$$

To solve this equation we isolate a time-independent part $(v_{s,0} - \epsilon) < 2c^2$ in the potential v_s , with $v_{s,0}$ an arbitrary function of \mathbf{r} and ϵ an arbitrary constant, so that we can rewrite,

$$\hat{X} = (2c^2 - v_{s,0} + \epsilon)^{-1} (c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} + \Xi(\hat{X})), \quad (4.43)$$

where we introduce

$$\Xi(\hat{X}) = [v_s - v_{s,0} + \epsilon - i\partial_t, \hat{X}] - \hat{X} (v_{s,0} - \epsilon + c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X}). \quad (4.44)$$

We can choose $(v_{s,0} - \epsilon)$ in such a way that $\Xi(\hat{X})$ is small when acting on ϕ , i.e.,

$$\Xi(\hat{X})\phi = (v_s - v_{s,0} + \epsilon - i\partial_t)\chi, \quad (4.45)$$

for electron-like states. For example we can choose $v_{s,0}$ such that $(v_s - v_{s,0})$ is small everywhere and ϵ close to the orbital energy of the relevant states. In this way Eq. (4.43) can be solved by iteration,

$$\hat{X}_n = (2c^2 - v_{s,0} + \epsilon)^{-1} (c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} + \Xi(\hat{X}_{n-1})). \quad (4.46)$$

If we insert an initial term \hat{X}_{-1} on the right-hand side of Eq. (4.46), then we obtain on the left-hand side the term \hat{X}_0 . We can then insert \hat{X}_0 on the right-side and obtain \hat{X}_1 and so on. If we take $\hat{X}_{-1} = 0$ then \hat{X}_0 is similar to the operator used in the stationary case,

$$\hat{X}_0 = (2c^2 - v_{s,0} + \epsilon)^{-1} c\boldsymbol{\sigma} \cdot \boldsymbol{\pi}. \quad (4.47)$$

Similar to the stationary case, the time-dependent Dirac equation can be reduced to a two-component one by using a unitary transformation U which leads to a transformed equation,

$$(U\hat{H}^D U^{-1} - U[i\partial_t, U^{-1}])\Phi(\mathbf{r}, t) = i\partial_t \Phi(\mathbf{r}, t), \quad (4.48)$$

where the transformed Hamiltonian is block diagonal. Here $\Phi(\mathbf{r}, t) = U\psi(\mathbf{r}, t)$. The upper-left part of the transformed Hamiltonian is the two-component time-dependent Foldy-Wouthuysen Hamiltonian,

$$\begin{aligned} \hat{H}^{FW} = & v_s + \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}} \times \left(c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} + \hat{X}^\dagger c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} - 2c^2 \hat{X}^\dagger \hat{X} - \hat{X}^\dagger [i\partial_t - v_s, \hat{X}] \right) \times \\ & \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}} - \sqrt{(1 + \hat{X}^\dagger \hat{X})} \times \left[i\partial_t - v_s, \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}} \right], \end{aligned} \quad (4.49)$$

where we have collected the terms containing the potential v_s together with the terms containing the time derivative $i\partial_t$. By using the equation of motion (4.42) to write $[i\partial_t - v_s, \hat{X}] = -[v_s - i\partial_t, \hat{X}] = c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} - 2c^2 \hat{X} - \hat{X} c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X}$, Eq. (4.49) can be written as

$$\begin{aligned} \hat{H}^{FW} = & v_s + c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} \\ & + \left[i\partial_t - v_s - c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X}, \sqrt{1 + \hat{X}^\dagger \hat{X}} \right] \times \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}}. \end{aligned} \quad (4.50)$$

To evaluate the commutator in the last line of Eq. (4.50) we express the square root $\sqrt{1 + \hat{X}^\dagger \hat{X}}$ in a Taylor expansion $\sum_{n=0}^{\infty} a_n (\hat{X}^\dagger \hat{X})^n$. We have that

$$\begin{aligned} \left[i\partial_t - v_s - c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X}, (\hat{X}^\dagger \hat{X})^n \right] = & \sum_{m=0}^{n-1} (\hat{X}^\dagger \hat{X})^m \left(\left[i\partial_t - v_s - c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X}, \hat{X}^\dagger \right] \hat{X} + \right. \\ & \left. \hat{X}^\dagger \left[i\partial_t - v_s - c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X}, \hat{X} \right] \right) (\hat{X}^\dagger \hat{X})^{n-m-1}. \end{aligned} \quad (4.51)$$

By using again Eq. (4.42) for $\left[i\partial_t - v_s, \hat{X} \right]$ and for $\left[i\partial_t - v_s, \hat{X}^\dagger \right] = -\left[i\partial_t - v_s, \hat{X} \right]^\dagger$, and by working out the other two commutators, we arrive at

$$\begin{aligned} \left[i\partial_t - v_s - c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X}, (\hat{X}^\dagger \hat{X})^n \right] = & \sum_{m=0}^{n-1} (\hat{X}^\dagger \hat{X})^m \left(\hat{X}^\dagger c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} - c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} \right) \times \\ & (\hat{X}^\dagger \hat{X})^{n-m-1} (1 + \hat{X}^\dagger \hat{X}). \end{aligned} \quad (4.52)$$

By combining (4.50) and (4.52) we arrive at the following expression for the time-dependent Foldy-Wouthuysen Hamiltonian,

$$\hat{H}^{FW} = v_s + \frac{1}{2} \left(c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} + \hat{X}^\dagger c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \right) + \hat{Y}, \quad (4.53)$$

where the operator \hat{Y} is given by

$$\begin{aligned} \hat{Y} = & \frac{1}{2} \left(c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} - \hat{X}^\dagger c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \right) \\ & - \sum_{n=0}^{\infty} a_n \sum_{m=0}^{n-1} (\hat{X}^\dagger \hat{X})^m \left(c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \hat{X} - \hat{X}^\dagger c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \right) \times \\ & (\hat{X}^\dagger \hat{X})^{n-m-1} \times \sqrt{1 + \hat{X}^\dagger \hat{X}}. \end{aligned} \quad (4.54)$$

The expression (4.53) shows that the time-dependent Foldy-Wouthuysen Hamiltonian is the sum of a Hermitian part similar to the stationary ZORA Hamiltonian (4.35) and a remainder \hat{Y} . In App. D we show that this remainder is Hermitian as well and of the first order in $(\hat{X}^\dagger \hat{X})$. If we neglect terms of the order of $\Xi(\hat{X})$ in the expression (4.43), then $\hat{X} = \hat{X}_0$ and $\hat{Y} = 0$. Using this approximation in Eq. (4.53) we obtain the time-dependent ZORA Hamiltonian,

$$\hat{H}^{ZORA} = v_s + \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \frac{c^2}{2c^2 - v_{s,0} + \epsilon} \boldsymbol{\sigma} \cdot \boldsymbol{\pi}. \quad (4.55)$$

4.2.3 Gauge invariance

The ZORA equation (4.35) is not gauge invariant under a gauge transformation

$$v_s(\mathbf{r}) \rightarrow v_s(\mathbf{r}) + \Delta, \quad (4.56)$$

with Δ a constant. As shown in Ref. [79] the ZORA equation for this potential will not have eigenvalues which are shifted by the same constant. The equation is, however, gauge invariant under the combined gauge transformation

$$\begin{aligned} \mathbf{A}_s(\mathbf{r}) &\rightarrow \mathbf{A}_s(\mathbf{r}) + \nabla\Lambda(\mathbf{r}), \\ \Phi^{ZORA}(\mathbf{r}) &\rightarrow \Phi^{ZORA}(\mathbf{r})e^{-i\Lambda(\mathbf{r})}, \end{aligned} \quad (4.57)$$

where $\Lambda(\mathbf{r})$ is any scalar function of position only. The time-dependent ZORA equation (4.55) is, instead, gauge invariant under the transformations

$$\begin{aligned} v_s(\mathbf{r}, t) &\rightarrow v_s(\mathbf{r}, t) + \frac{\partial\Lambda(\mathbf{r}, t)}{\partial t}, \\ \mathbf{A}_s(\mathbf{r}, t) &\rightarrow \mathbf{A}_s(\mathbf{r}, t) + \nabla\Lambda(\mathbf{r}, t), \\ \Phi^{ZORA}(\mathbf{r}, t) &\rightarrow \Phi^{ZORA}(\mathbf{r}, t)e^{-i\Lambda(\mathbf{r}, t)}, \end{aligned} \quad (4.58)$$

provided that the potential $(v_{s,0}(\mathbf{r}) - \epsilon)$ is kept fixed. Here $\Lambda(\mathbf{r}, t)$ is now a scalar function of space and time. This means that the time-dependent ZORA equation is gauge-invariant, but the results depend on the choice of $(v_{s,0}(\mathbf{r}) - \epsilon)$. In practical applications one can demand the potential $v_s(\mathbf{r}, t_0)$ to go to zero at infinity. In this case one can choose $v_{s,0}(\mathbf{r}) = v_s(\mathbf{r}, t_0) - v_s(\mathbf{r} = \infty, t_0)$ and $\epsilon = 0$, where v_s is calculated in the Coulomb gauge ($\nabla \cdot \mathbf{A}_s(\mathbf{r}, t_0) = 0$), and the gauge-invariance (4.58) is guaranteed, but it still depends on our particular choice for $(v_{s,0}(\mathbf{r}) - \epsilon)$.

4.2.4 The relativistic ZORA density and current operators

The unitary transformation that is used to reduce the four-component Dirac equation to an effective two-component pseudorelativistic equation represents a picture change: we pass from the Dirac picture to a new picture, which is appropriately called Schrödinger picture. This picture change requires that not only the wavefunction is transformed but also the operators, in order to keep the physics unaltered. For example, the position operator $\hat{\mathbf{r}}$ represents in the new picture a new physical observable which is called the mean position or mass position $\hat{\mathbf{r}}_{mass}$ of the electron [81,82], while the transformed $U\hat{\mathbf{r}}U^{-1}$ operator represents the original position in the new picture. Neglecting the picture change results in an error, which is usually small but

visible for core states [83]. We define the four-current operator in the Dirac picture as

$$\hat{j}_\mu^D(\mathbf{r}) = c \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \alpha^\mu, \quad (4.59)$$

where the scalar component is the density operator $\hat{\rho}^D(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \alpha^0$, and the vector component the current operator $\hat{\mathbf{j}}^D(\mathbf{r}) = c \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \boldsymbol{\alpha}$. If we transform $\hat{\rho}^D(\mathbf{r})$, the Foldy-Wouthuysen density operator $\hat{\rho}^{FW}$ is given by

$$\hat{\rho}^{FW}(\mathbf{r}) = \sum_i \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}} \left(\delta(\mathbf{r} - \mathbf{r}_i) + \hat{X}^\dagger \delta(\mathbf{r} - \mathbf{r}_i) \hat{X} \right) \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}}. \quad (4.60)$$

If we take the operator \hat{X} to be the ZORA operator \hat{X}_0 and we neglect terms of order of $(\hat{X}^\dagger \hat{X})$ in Eq. (4.60), the approximate ZORA density operator is simply

$$\hat{\rho}^{ZORA}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (4.61)$$

This amounts to neglect the picture change for the density operator, in line with van Lenthe *et al.* [79], who showed that the approximate ZORA density reproduces very well the Dirac density, in particular for the valence region.

For the transformed current operator we proceed in a similar way, and the Foldy-Wouthuysen current operator $\hat{j}_\mu^{FW}(\mathbf{r})$ is given by

$$\hat{j}_\mu^{FW}(\mathbf{r}) = \sum_i \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}} \left(c \delta(\mathbf{r} - \mathbf{r}_i) \sigma_\mu \hat{X} + c \hat{X}^\dagger \delta(\mathbf{r} - \mathbf{r}_i) \sigma_\mu \right) \frac{1}{\sqrt{1 + \hat{X}^\dagger \hat{X}}}. \quad (4.62)$$

In the zeroth-order regular approximation the ZORA current operator is given by

$$\hat{j}_\mu^{ZORA}(\mathbf{r}) = \sum_i \left(\delta(\mathbf{r} - \mathbf{r}_i) \sigma_\mu \frac{K(\mathbf{r}_i)}{2} (\boldsymbol{\sigma} \cdot \boldsymbol{\pi}_i) + (\boldsymbol{\sigma} \cdot \boldsymbol{\pi}_i) \frac{K(\mathbf{r}_i)}{2} \delta(\mathbf{r} - \mathbf{r}_i) \sigma_\mu \right). \quad (4.63)$$

By exploiting the property of the Pauli matrices, $\sigma_\mu \sigma_\nu = \delta_{\mu\nu} + i \sum_\tau \epsilon_{\mu\nu\tau} \sigma_\tau$, this expression can be rearranged as

$$\begin{aligned} \hat{j}_\mu^{ZORA}(\mathbf{r}) &= \sum_{i\nu} \left(\delta(\mathbf{r} - \mathbf{r}_i) \frac{K(\mathbf{r}_i)}{2} \sigma_\mu \sigma_\nu \pi_{i\nu} + \sigma_\nu \pi_{i\nu} \sigma_\mu \frac{K(\mathbf{r}_i)}{2} \delta(\mathbf{r} - \mathbf{r}_i) \right) \\ &= \sum_{i\nu} \left(\delta(\mathbf{r} - \mathbf{r}_i) \frac{K(\mathbf{r}_i)}{2} (\delta_{\mu\nu} + i \sum_\tau \epsilon_{\mu\nu\tau} \sigma_\tau) \pi_{i\nu} + \right. \\ &\quad \left. (\delta_{\mu\nu} + i \sum_\tau \epsilon_{\nu\mu\tau} \sigma_\tau) \pi_{i\nu} \frac{K(\mathbf{r}_i)}{2} \delta(\mathbf{r} - \mathbf{r}_i) \right) \\ &= \sum_i \left(\delta(\mathbf{r} - \mathbf{r}_i) \frac{K(\mathbf{r}_i)}{2} \pi_{i\mu} + \pi_{i\mu} \frac{K(\mathbf{r}_i)}{2} \delta(\mathbf{r} - \mathbf{r}_i) \right) + \\ &\quad \left(\delta(\mathbf{r} - \mathbf{r}_i) \frac{K(\mathbf{r}_i)}{2} i(\mathbf{p}_i \times \boldsymbol{\sigma})_\mu - i(\mathbf{p}_i \times \boldsymbol{\sigma})_\mu \frac{K(\mathbf{r}_i)}{2} \delta(\mathbf{r} - \mathbf{r}_i) \right). \end{aligned} \quad (4.64)$$

From this expression it follows that the approximate ZORA current operator can be decomposed into a paramagnetic, a diamagnetic, and a spin contribution, given by

$$\hat{\mathbf{j}}_p(\mathbf{r}) = -\frac{i}{2}K(\mathbf{r}) \sum_i \left[\delta(\mathbf{r} - \mathbf{r}_i) \nabla_i - \nabla_i^\dagger \delta(\mathbf{r} - \mathbf{r}_i) \right], \quad (4.65)$$

$$\hat{\mathbf{j}}_d(\mathbf{r}) = \frac{1}{c}K(\mathbf{r}) \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{A}_s(\mathbf{r}_i, t), \quad (4.66)$$

$$\hat{\mathbf{j}}_s(\mathbf{r}) = K(\mathbf{r}) \nabla \times \hat{\mathbf{s}}(\mathbf{r}), \quad (4.67)$$

where

$$\hat{\mathbf{s}}(\mathbf{r}) = \frac{1}{2} \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \boldsymbol{\sigma}. \quad (4.68)$$

It now becomes clear that the composition of the ZORA current-density is similar to the one obtained in the Gordon decomposition of the Dirac current (see Eq. (4.20)-(4.24)). Note that one arrives at the same expression (4.64) for the ZORA current operator by starting from the following anticommutator,

$$\hat{\mathbf{j}}^{ZORA}(\mathbf{r}) = \frac{1}{2} \sum_i \{ \hat{\mathbf{v}}_i^{ZORA}, \delta(\mathbf{r} - \mathbf{r}_i) \}, \quad (4.69)$$

with the approximate ZORA velocity operator given as

$$\hat{\mathbf{v}}_i^{ZORA} = -i [\mathbf{r}_i, H_i^{ZORA}]. \quad (4.70)$$

This relation guarantees the validity of the Thomas-Reiche-Kuhn f -sum rule, which is used in the form of the conductivity sumrule in our response calculations.

4.2.5 Linear response

We can now combine the ZORA formalism with the time-dependent current-density formulation of the linear response of solids to a macroscopic field given in chapter 3. We start from a Kohn-Sham system in the ground-state described by the stationary ZORA Hamiltonian

$$\hat{H}_0^{ZORA} = \sum_i \left(v_{eff,0}(\mathbf{r}_i) + \boldsymbol{\sigma} \cdot \mathbf{p}_i \frac{c^2}{2c^2 - v_{eff,0}(\mathbf{r}_i)} \boldsymbol{\sigma} \cdot \mathbf{p}_i \right), \quad (4.71)$$

and we study the response of the system to small perturbing potentials $\delta v_{eff}(\mathbf{r}, t)$ and $\delta \mathbf{A}_{eff}(\mathbf{r}, t)$. To do this we consider the time-dependent ZORA Hamiltonian (4.55) with

$$\begin{aligned} v_{eff}(\mathbf{r}, t) &= v_{eff,0}(\mathbf{r}) + \delta v_{eff}(\mathbf{r}, t), \\ \mathbf{A}_{eff}(\mathbf{r}, t) &= \delta \mathbf{A}_{eff}(\mathbf{r}, t), \end{aligned}$$

where the effective potentials have been described in chapter 3. We then have

$$\begin{aligned}
\hat{H}^{ZORA}(t) &= \sum_i \left\{ \boldsymbol{\pi}_i \cdot \frac{K(\mathbf{r}_i)}{2} \boldsymbol{\pi}_i + i\boldsymbol{\sigma} \left(\boldsymbol{\pi}_i \times \frac{K(\mathbf{r}_i)}{2} \boldsymbol{\pi}_i \right) + v_{eff,0}(\mathbf{r}_i) + \delta v_{eff}(\mathbf{r}_i, t) \right\} \\
&= \sum_i \left\{ \mathbf{p}_i \cdot \frac{K(\mathbf{r}_i)}{2} \mathbf{p}_i + v_{eff,0}(\mathbf{r}_i) + \delta v_{eff}(\mathbf{r}_i, t) \right. \\
&\quad + \frac{1}{2c} [\mathbf{p}_i \cdot K(\mathbf{r}_i) \delta \mathbf{A}_{eff}(\mathbf{r}_i, t) + \delta \mathbf{A}_{eff}(\mathbf{r}_i, t) \cdot K(\mathbf{r}_i) \mathbf{p}_i] + \frac{K(\mathbf{r}_i)}{2c} \delta \mathbf{A}_{eff}^2(\mathbf{r}_i, t) \\
&\quad \left. + \frac{i}{2c} [\delta \mathbf{A}_{eff}(\mathbf{r}_i, t) K(\mathbf{r}_i) (\mathbf{p}_i \times \boldsymbol{\sigma}) - (\mathbf{p}_i \times \boldsymbol{\sigma}) K(\mathbf{r}_i) \delta \mathbf{A}_{eff}(\mathbf{r}_i, t)] \right\}. \quad (4.72)
\end{aligned}$$

This expression can be arranged further as follows,

$$\begin{aligned}
\hat{H}^{ZORA}(t) &= \sum_i \left(-\nabla_i \cdot \frac{K(\mathbf{r}_i)}{2} \nabla_i + v_{eff,0}(\mathbf{r}_i) \right) + \int \left\{ d\mathbf{r} \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta v_{eff}(\mathbf{r}, t) \right. \\
&\quad - \frac{i}{2c} \sum_i \left(\delta(\mathbf{r} - \mathbf{r}_i) K(\mathbf{r}_i) \nabla_i - \nabla_i^\dagger K(\mathbf{r}_i) \delta(\mathbf{r} - \mathbf{r}_i) \right) \delta \mathbf{A}_{eff}(\mathbf{r}, t) \\
&\quad \left. + \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \frac{K(\mathbf{r}_i)}{2c^2} \delta \mathbf{A}_{eff}^2(\mathbf{r}, t) + \frac{K(\mathbf{r})}{c} (\nabla \times \hat{\mathbf{s}}(\mathbf{r})) \delta \mathbf{A}_{eff}(\mathbf{r}, t) \right\} d\mathbf{r}, \quad (4.73)
\end{aligned}$$

where we have considered $\mathbf{p} = -i\nabla$, $v_{eff}(\mathbf{r}_i, t) = \int \delta(\mathbf{r} - \mathbf{r}_i) v_{eff}(\mathbf{r}, t) d\mathbf{r}$, and $\mathbf{A}_{eff}(\mathbf{r}_i, t) = \int \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{A}_{eff}(\mathbf{r}, t) d\mathbf{r}$. The first two terms on the right-hand side of Eq. (4.73) represent the ground-state ZORA Hamiltonian (4.71), whereas the remaining terms represent the perturbation Hamiltonian $\delta \hat{h}(t)$, which can be written as

$$\begin{aligned}
\delta \hat{h}(t) &= \int \left(\hat{\rho}(\mathbf{r}) \delta v_{eff}(\mathbf{r}, t) + \frac{1}{c} \hat{\mathbf{j}}_p(\mathbf{r}) \cdot \delta \mathbf{A}_{eff}(\mathbf{r}, t) \right. \\
&\quad \left. + \frac{1}{2c^2} \hat{\rho} K(\mathbf{r}) \mathbf{A}_{eff}^2(\mathbf{r}, t) + \frac{1}{c} \hat{\mathbf{j}}_s(\mathbf{r}) \cdot \delta \mathbf{A}_{eff}(\mathbf{r}, t) \right) d\mathbf{r}. \quad (4.74)
\end{aligned}$$

Note that the last term on the right-hand side of Eq. (4.74) represents the perturbation due to a magnetic field $\delta \mathbf{B}_{eff}(\mathbf{r}, t) = \nabla \times \delta \mathbf{A}_{eff}(\mathbf{r}, t)$,

$$\begin{aligned}
\frac{1}{c} \hat{\mathbf{j}}_s(\mathbf{r}) \cdot \delta \mathbf{A}_{eff}(\mathbf{r}, t) &= -\frac{1}{c} \hat{\mathbf{s}}(\mathbf{r}) (\nabla \times K(\mathbf{r}) \delta \mathbf{A}_{eff}(\mathbf{r}, t)) \\
&= -\frac{1}{c} \hat{\mathbf{s}}(\mathbf{r}) (\nabla K(\mathbf{r}) \times \delta \mathbf{A}_{eff}(\mathbf{r}, t)) - \frac{1}{c} K(\mathbf{r}) \hat{\mathbf{s}}(\mathbf{r}) \cdot \delta \mathbf{B}_{eff}(\mathbf{r}, t). \quad (4.75)
\end{aligned}$$

We will not treat response to magnetic fields in this thesis, thus $\delta \mathbf{B}_{eff}(\mathbf{r}, t) = 0$. Furthermore, since for the systems of interest here $K(\mathbf{r}) \simeq 1$ and $\nabla v_{eff,0}(\mathbf{r}) \ll 2c^2$, it follows that $\nabla K(\mathbf{r}) = K^2(\mathbf{r}) \nabla v_{eff,0}(\mathbf{r}) / 2c^2 \ll 0$. The last term in (4.74) will thus give

a very small contribution to the perturbation. If we do not include spin-orbit coupling in the time-dependent ZORA Hamiltonian, and we consider only scalar relativistic effects, then this last term does not appear in the perturbation. We can conclude that the difference in the perturbation within the scalar ZORA and the ZORA approaches is small, and that the main effect of the spin-orbit coupling on the linear response is due to the changes in the ground-state orbital energies. It now becomes clear how we can solve the linear response for a Kohn-Sham system within the ZORA approximation. We first solve the time-independent ZORA equation (4.71) to obtain the ground-state orbitals and orbital energies. Given the perturbation (4.74), in which we retain only terms linear in the field, we can then evaluate the various response functions and solve self-consistently the equations describing the induced density and induced current-density.

